

PATENT SPECIFICATION

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(54) POLYMERIZATION OF DIOLEFINS

(71) We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improvement in a method for producing an active catalyst for the polymerization of certain diolefins or mixtures of diolefins to polymers having high cis-1,4 content. More specifically, the invention relates to the polymerization of at least one conjugated diolefin to polymers having a high cis-1,4 content. Still more specifically it relates to improved catalysts useful for such polymerization.

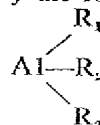
It is known that polymerization of conjugated diolefins can be promoted by contacting the diolefin with a catalyst system comprising (A) a trialkylaluminum or alkyl-aluminum hydride, (B) a compound of a metal of the Group III-B of the Periodic Table of the Elements and (C) an alkyl-aluminum halide. Such catalyst systems polymerize conjugated diolefins, in good yields, to produce polymers having very high cis-1,4 content, which are particularly useful as extenders or substitutes for natural rubber. However, these catalyst systems have the disadvantage that relatively long reaction times are required to give highly economical yields of polymer. (Wherever reference is made herein to the Periodic Table of the Elements, it is to be construed as being a reference to that version of the Periodic Table published in the 39th Edition of the "Handbook of Chemistry and Physics" on pages 400 to 401 by the Chemical Rubber Publishing Co., of Cleveland, Ohio, U.S.A.)

It is an objective of this invention to provide a method whereby conjugated diolefins such as butadiene or isoprene can be polymerized to a high content or cis-1,4-

polybutadiene or polyisoprene, that is, a cis content greater than 85%. Another object is to provide a method whereby mixtures of butadiene and isoprene, mixtures of butadiene and other conjugated diolefins, mixtures of isoprene and other conjugated diolefins and mixtures of other conjugated diolefins can be polymerized to form the corresponding copolymers of high cis-1,4 structure. Another object is to provide a catalyst system by which these polymerizations may be accomplished. Another object is to provide a method of preparing the catalyst system by which these polymerizations may be carried out at increased rates of reaction. Other objects will become apparent as the description proceeds.

According to the invention, an improvement has been obtained in a process of polymerizing conjugated diolefins to form polymers exhibiting a high cis-1,4 content, which process comprises polymerizing at least one conjugated diolefin by contacting, under solution polymerization conditions, at least one conjugated diolefin with a catalyst comprising (A) a compound selected from organoaluminum compounds containing at least one carbon to aluminum bond, (B) a metallic coordination compound, the metal of which is selected from the metals of Group III-B of the Periodic Table having atomic numbers of 21, 39 and 57 to 71 inclusive, and (C) at least one compound containing one or more halide ions, the improvement comprising preforming and aging the catalyst system with at least one conjugated diolefin in an amount which gives a mole ratio of diolefin to the Group III-B metal compound ranging from 0.2/1 to 3000/1.

The first or (A) catalyst component, which is an organoaluminum compound containing at least one carbon to aluminum bond, may be defined by the formula:



in which R_1 is selected from alkyl (including cycloalkyl), alkoxy, aryl, alkaryl, arylalkyl radicals and hydrogen; R_2 is selected from alkyl (including cycloalkyl), aryl, alkaryl, arylalkyl radicals and hydrogen and R_3 is selected from alkyl (including cycloalkyl), aryl, alkaryl and arylalkyl radicals. Representative of the compounds corresponding to this definition are: diethylaluminum hydride, di-n-propylaluminum hydride, di-n-butylaluminum hydride, diisobutylaluminum hydride, diphenylaluminum hydride, di-p-tolylaluminum hydride, dibenzylaluminum hydride, phenylethylaluminum hydride, phenyl-n-propylaluminum hydride, p-tolyethylaluminum hydride, p-tolyl-n-propylaluminum hydride, p-tolylisopropylaluminum hydride, benzylethylaluminum hydride, benzyl-n-propylaluminum hydride, and benzylisopropylaluminum hydride and other organoaluminum hydrides. Also included are ethylaluminum dihydride, butylaluminum dihydride, isobutylaluminum dihydride, octylaluminum dihydride, amylaluminum dihydride and other organoaluminum dihydrides. Also included are diethylaluminum ethoxide and dipropylaluminum ethoxide. Also included are trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-pentylaluminum, trihexylaluminum, tricyclohexylaluminum, trioctylaluminum, triphenylaluminum, tri-p-tolylaluminum, tri-benzylaluminum, ethyldiphenylaluminum, ethyl-di-p-tolylaluminum, ethyldibenzylaluminum, diethylphenylaluminum, diethyl-p-tolylaluminum, diethylbenzylaluminum and other triorganoaluminum compounds.

The second or (B) catalyst component of the catalyst system is a metallic coordination compound of metals of Group III-B of the Periodic Table having atomic numbers of 21, 39 and 57 through 71 inclusive. The metal ion forms the central core or atom to which two or more ligand-type groups or atoms are joined. The resulting compound may be known as a coordination compound. For the present invention, the most useful of these coordination compounds comprise metals of Group III-B and ligands represented by organic groups containing from 1 to 20 carbon atoms. These compounds may be symbolically represented as ML_n , wherein M represents the metal ion of Group III-B and L represents the organic ligand and n is an integer of 2 or greater.

Representative Group III-B metals useful in the invention include scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Of these, cerium, neodymium and lan-

thanum having atomic numbers of 58, 68 and 71 respectively are the most preferred.

The organic portion of the coordination compound includes organic-type ligands containing from 1 to 20 carbon atoms. These ligands may be of the monovalent and bidentate or divalent and bidentate form. The functional groups which may be on these ligands are such groups as tertiary nitrogen, formyl, carbonyl, oxy, alkoxy, alkoxycarbonyl, amino, alkimino and hydroxyl. Representative of such ligands are o-hydroxyaldehydes such as salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2-hydroxy-3-naphthaldehyde; o-hydroxyphenones such as 2'-hydroxyacetophenone, 2'-hydroxybutyrophenone and 2'-hydroxypropio-phenone; aminophenols such as o-aminophenol, N-methyl o-aminophenol and N-ethyl o-aminophenol; hydroxy esters such as ethyl salicylate, propyl salicylate and butyl salicylate; phenolic compounds such as 2-hydroxyquinoline and 8-hydroxyquinoline; β -diketones such as acetylacetone, benzoylacetone, propionylacetone, isobutyrylacetone, valerylacetone and ethylacetylacetone; monocarboxylic acids such as acetic acid, propionic acid, valeric acid, hexanoic acid, 2-ethylhexanoic acid, neodecanoic acid, lauric acid and stearic acid; ortho dihydric phenols such as pyrocatechol; alkylene glycols such as ethylene glycol, propylene glycol, trimethylene glycol and tetramethylene glycol; dicarboxylic acids such as oxalic acid, malonic acid, maleic acid, succinic acid and o-phthalic acid; alkylated derivatives of the above described dicarboxylic acids; phenolic ethers such as o-hydroxyanisole and o-hydroxyethyl phenyl ether.

Representative compounds of the Group III-B metals which may be useful in this invention include cerium acetylacetonate, cerium naphthenate, cerium neodecanoate, cerium octanoate, tris-salicylaldehyde cerium, cerium tris(8-hydroxyquinolate), lanthanum naphthenate, lanthanum octanoate, neodymium neodecanoate, neodymium octanoate, yttrium acetylacetonate, yttrium octanoate, dysprosium octanoate and other Group III-B metals complexed with ligands containing from 1 to 20 carbon atoms.

The third or (C) catalyst component of this invention is a compound containing one or more halide ions. Representatives of the halide ions which are within the scope of this invention include bromide ion, chloride ion, fluoride ion and iodide ion and the presence of one or more of these ions is essential in the catalyst system. These halide ions may be introduced as (1) hydrogen halides; (2) alkyl, aryl, alkaryl, aralkyl and cycloalkyl metal halides wherein the metal is selected from Groups II, III-A and IV-A of the Periodic Table; (3) halides of metals of Groups III, IV, V, VI-B and

VIII of the Periodic Table and (4) organometallic halides wherein the metal of the organometallic halide is selected from metals of Group III-B of the Periodic Table having atomic numbers of 21, 39 and 57 to 71 inclusive.

Representative examples of such compounds containing a halide ion include (1) hydrogen bromide, hydrogen chloride and hydrogen iodide; (2) ethylmagnesium bromide, butylmagnesium bromide, phenylmagnesium bromide, methylmagnesium chloride, butylmagnesium chloride, ethylmagnesium iodide, phenylmagnesium iodide, diethylaluminum bromide, diisobutylaluminum bromide, methylaluminum sesquibromide, diethylaluminum chloride, ethylaluminum dichloride, ethylaluminum sesquichloride, diisobutylaluminum chloride, isobutylaluminum dichloride, dihexylaluminum chloride, cyclohexylaluminum dichloride, phenylaluminum dichloride, didodecylaluminum chloride, diethylaluminum fluoride, dibutylaluminum fluoride, diethylaluminum iodide, dibutylaluminum iodide, phenylaluminum diiodide, trimethyltin bromide, triethyltin chloride, dibutyltin dichloride, butyltin trichloride, diphenyltin dichloride and tributyltin iodide; (3) aluminum bromide, aluminum chloride, aluminum iodide, antimony pentachloride, antimony trichloride, boron tribromide, boron trichloride, ferric chloride, gallium trichloride, molybdenum pentachloride, phosphorus tribromide, phosphorus pentachloride, stannic chloride, titanium tetrachloride, titanium tetraiodide and tungsten hexachloride; and (4) *t*-butylsalicylaldehydocerium(III)chloride, salicylaldehydocerium(III)chloride, 5-cyclohexylsalicylaldehydocerium(III)chloride, 2-acetylphenolatocerium(III)chloride, oxalatocerium(III)chloride and oxalatocerium(III)bromide. The halide ions in the third or (C) component of this invention are labile halide ions.

The conjugated diolefins which may be polymerized in accordance with the above described catalyst system are those aliphatic conjugated diolefins commonly employed in the preparation of synthetic rubber. Representative but not exclusive of such conjugated diolefins are 1,3-dienes such as butadiene-1,3; substituted 1,3-butadienes such as isoprene; 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene; 2-propyl-1,3-butadiene; 2-hexyl-1,3-butadiene; 2,3-diethyl-1,3-butadiene, 2,3-dibutyl-1,3-butadiene; 2-decyl-1,3-butadiene and other substituted butadienes in which the substituent group contain up to 12 carbon atoms. However, when the substituent groups are more than about 8 carbon atoms, the 1,3-butadienes should be mono-substituted.

The known techniques normally used in the preparation of an active catalyst are the

"in situ" and the "preformed" techniques. By "in situ" is meant that the catalyst components are added separately to the monomer to be polymerized. By "preformed" is meant the manner in which the catalyst components are mixed together prior to exposure of any of the components to the monomer to be polymerized. It is also known that when employing the type of catalyst system described in this invention, the presence of monomer is not essential to the formation of an active catalyst species, thus, facilitating the use of "preformed" catalysts. Also, it is known that freshly "preformed" catalysts are frequently more active than catalysts which have been allowed to age before use.

The present invention employs a "preformed" catalyst technique but one which has been greatly improved by "preforming" the catalyst components in the presence of small amounts of a conjugated diolefin and generally the diolefin that is to be polymerized. It has been found that when the catalyst is "preformed" in the presence of a conjugated diolefin, polymerization rates are increased up to 100% or greater. It has also been found that when catalysts that have been "preformed" in the presence of a conjugated diolefin are allowed to age over a period of time ranging from a minute to 30 days before use, at temperatures ranging from 0°C. to 100°C., catalyst activity is also increased.

Usually the catalyst is prepared by mixing the conjugated diolefin and the catalyst components in the following preferred order: (1) inert solvent, (2) diolefin, (3) an organoaluminum compound such as trialkylaluminum or dialkylaluminum hydride, (4) Group III-B metal compound and (5) a compound containing a halide ion. Another preferred order of mixing the various components is (1) inert solvent, (2) an organoaluminum compound such as trialkylaluminum or dialkylaluminum hydride, (3) diolefin, (4) a compound containing a halide ion and (5) a Group III-B metal compound. These preferred orders of mixing the various components, which comprise the active catalyst, are not to be interpreted as excluding other orders of mixing; however, it is generally preferred that the organoaluminum compound always be added prior to the addition of the halide in order to obtain optimum results.

The conjugated diolefins which are added in small amounts during the "preforming" of the catalyst components to give the improved catalyst system described above, are those aliphatic conjugated diolefins commonly employed in the preparation of synthetic rubber. Representative but not exclusive of such conjugated diolefins are 1,3-dienes such as butadiene-1,3; substituted 1,3-

butadienes such as isoprene; 2,3-dimethyl-1,3-butadiene; 2-ethyl-1,3-butadiene; 2-propyl-1,3-butadiene; 2-hexyl-1,3-butadiene; 2,3-diethyl-1,3-butadiene; 2,3-dibutyl-1,3-butadiene; 2-decyl-1,3-butadiene and other substituted butadienes in which the substituent groups contain up to 12 carbon atoms. However, when the substituent groups are more than 8 carbon atoms, the 1,3-butadiene should be mono-substituted.

By the term "inert solvent" is meant that the solvent does not adversely affect the catalyst or its individual components. Such solvents are usually aliphatic, aromatic or cycloaliphatic hydrocarbons, representative of which are pentane, hexane, heptane, benzene, toluene and cyclohexane.

The proportions of the components of the polymerization catalyst composition of this invention can be varied widely. When the halide ion of the halogen containing compound is bromide, chloride or iodide ion, the atomic ratio of the halide ion to the Group III-B metal can vary from 0.1/1 to 6/1. A more preferred ratio is from 0.5/1 to 3.5/1 and the most preferred ratio is substantially 2/1. However, when the halide ion of the halogen-containing compound is fluoride ion, the ratio of the fluoride ion to the Group III-B metal ion ranges from 20/1 to 80/1 with the most preferred ratio being 30/1 to 60/1. The molar ratio of the organoaluminum compound to Group III-B metal can range from 4/1 to 200/1 with the most preferred range being from 8/1 to 100/1. The molar ratio of diolefin to Group III-B metal ranges from 0.2/1 to 3000/1 with the most preferred range being from 5/1 to 500/1.

The amount of catalyst charged to the reaction system can be varied over a wide range; the sole requirement being that a catalytic amount of the catalyst composition, sufficient to cause polymerization of the diolefin, be present in the reaction system. Low concentrations of catalyst are desirable in order to minimize ash problems. It has been found that polymerizations will occur when the catalyst level of the Group III-B metal varies between 0.05 and 1.0 millimoles of Group III-B metal per 100 grams of monomer. A preferred ratio is between 0.15 and 0.3 millimoles of Group III-B metal per 100 grams of monomer.

The concentration of the total catalyst system employed of course, depends upon factors such as purity of the system, polymerization rate desired, temperature and other factors. Therefore, specific concentrations cannot be set forth except to say that catalytic amounts are used.

The polymerization of the diolefin can be carried out by conventional solution polymerization procedures employing suit-

able inert solvents. By the term "inert solvent" is meant that the solvent or diluent does not enter into the structure of or affect adversely the resulting polymer. Such solvents are usually aliphatic, aromatic or cycloaliphatic hydrocarbons, representative of which are pentane, hexane, heptane, benzene, toluene and cyclohexane. The solvent/monomer volume ratio may be varied over a wide range. Up to 20 or more to 1 volume ratio of solvent to monomer can be employed. It is usually preferred, or more convenient, to use a solvent/monomer ratio of 3/1 to 6/1.

Temperatures at which the polymerization reaction is carried out can be varied over a wide range. Usually the temperature can be varied from extremely low temperatures such as -60°C . up to high temperatures such as 150°C . or higher. Thus, the temperature is not a critical factor of the invention. It is generally preferred, however, to conduct the reaction at a temperature in the range of from -30°C . to 80°C . The pressure at which the polymerization is carried out can also be varied over a wide range. The reaction can be conducted at atmospheric pressure or, if desired, it can be carried out at sub-atmospheric or super-atmospheric pressure. Generally, a satisfactory polymerization is obtained when the reaction is carried out at about autogeneous pressure, developed by the reactants under the operating conditions used.

The practice of this invention is further illustrated by reference to the following examples which are intended to be representative rather than restrictive of the scope of this invention, and with which are included, for the purposes of comparison only, certain examples lying outside the scope of the invention.

The inherent viscosity, which is also known as dilute solution viscosity (DSV), was determined in toluene at 30°C . for a number of the polymers reported herein and is an indication of their relative molecular weights. The percent cis-1,4 content of a number of the polymers was determined from infra-red diffraction patterns obtained on these polymers.

EXAMPLE I

Preparation of Preformed Catalysts

The benzene solvent was dried by passing it through a silica gel column under a nitrogen atmosphere. A series of catalysts containing increasing amounts of butadiene was prepared by adding the appropriate amounts of dry benzene, butadiene, diisobutylaluminum hydride (DIBAH), cerium octanoate (CeOct) and ethylaluminum dichloride (EADC) to five 4-ounce bottles. These catalysts are designated A, B, C, D and E respectively. Each catalyst was

allowed to age at room temperature (25°C.) for a period of one hour, one day, three days and seven days prior to its use. The

table below gives all pertinent data as to the quantities of each of the catalyst components used.

TABLE 1

Catalyst	Millimoles					Mole Ratio Bd/Ce
	Benzene	Butadiene	DIBAH	CeOct	EADC	
10 A	1072	0	5.37	0.27	0.27	0/1
B	1060	2.72	5.37	0.27	0.27	10/1
C	1036	8.21	5.37	0.27	0.27	30/1
D	1010	13.71	5.37	0.27	0.27	50/1
E	985	19.1	5.37	0.27	0.27	70/1

- 15 Catalyst A is not intended as an example of the invention since it does not include the requisite diolefin.

EXAMPLE II

20 A series of polymerizations was carried out on a premix of butadiene as a 21% by weight solution in hexane in four ounce bottles. The amount of preformed catalyst which was prepared as in Example I employed in these polymerizations was the same in each run and contained 4 millimoles of diisobutylaluminum hydride, 0.2 millimole of cerium octanoate and 0.2 millimole of ethylaluminum dichloride per 100 grams of butadiene charged. The control run, which was an in situ catalyst preparation, employed the same amounts of the catalyst components except no butadiene was employed in the preparation of this catalyst because the catalyst was not preformed and

each catalyst component was injected into the polymerization mixture separately. The bottles were tumbled in a bath maintained at 50°C. for the reaction times indicated in Tables IIa and IIb. The polymerizations were deactivated by the addition of a suitable stopping agent and antioxidant. Polymer yields and dilute solution viscosities are reported in Tables IIa and IIb. On certain of these polymers the percentage of cis-1,4 content was determined and is reported in Table IIc. In Tables IIa, b and c, catalyst A is not intended as an example of the invention since it was not preformed and aged in the presence of a diolefin, but is included for the purposes of comparison only.

TABLE IIa

Catalyst	Mole Ratio Bd/Ce	Catalyst Aging Time			
		1 hr.	1 day	3 days	7 days
		Reaction Time			
		45 min.	30 min.	30 min.	30 min.
55 Control ^(a)	0:1	16	11	9	9
A ^(b)	0:1	29	29	28	28
B	10:1	37	58	55	58
60 C	30:1	42	61	68	69
D	50:1	43	63	68	76
E	70:1	42	62	68	76

^(a) — "in situ" catalyst system

^(b) — "Preformed" catalysts A through E from Example I

TABLE IIb

5	Catalyst	Mole Ratio Bd/Ce	Catalyst Aging Time			
			1 hr.	1 day	3 days	7 days
			Reaction Time			
10			45 min.	30 min.	30 min.	30 min.
			Dilute Solution Viscosity			
	Control ^(a)	0:1	2.29	ND	ND	2.67
	A ^(b)	0:1	2.13	3.12	3.61	3.88
	B	10:1	ND ^(c)	ND	3.75	4.21
	C	30:1	2.05	ND	ND	4.40
	D	50:1	ND	ND	3.33	4.28
	E	70:1	1.81	2.52	2.82	3.92

^(a) — "in situ" catalyst addition
^(b) — "Preformed" catalysts A through E from Example I
^(c) — Not Determined.

TABLE IIc

20	Catalyst	Mole Ratio Bd/Ce	Catalyst Aging Time			
			1 hr.	1 day	3 days	7 days
			Reaction Time			
25			45 min.	30 min.	30 min.	30 min.
			% cis-1,4 content			
	Control ^(a)	0:1	ND ^(c)	ND	ND	97.7
	A ^(b)	0:1	97.1	ND	ND	98.6
	B	10:1	ND	ND	ND	98.6
	D	50:1	ND	ND	ND	98.7
	E	70:1	96.8	97.8	ND	ND

^(a) — "in situ" addition of catalyst
^(b) — "Preformed" catalysts A through E from Example I
^(c) — Not Determined.

EXAMPLE III

Three series of polymerizations were conducted in 4-ounce bottles employing a pre-mix solution containing 20 weight percent of butadiene in hexane. Two preformed catalysts and one "in situ" catalyst were used to polymerize the butadiene. One of the preformed catalysts (designated as the A catalyst), was preformed in the presence of isoprene and the other preformed catalyst (designated as the B catalyst), was preformed in the presence of butadiene. The charge of the preformed A and B catalysts employed to polymerize the butadiene contained 12 millimoles of conjugated diolefin, 8 millimoles of diisobutylaluminum hydride (DIBAH), 0.4 millimole of cerium octano-

ate (Ce Oct) and 0.4 millimole of ethylaluminum dichloride (EADC). The same charge described above was added to all the bottles. The same amounts of the individual catalyst components were also employed in the "in situ" technique of charging catalyst except additional diolefin was not added. The "in situ" technique was used as a control. The preformed catalysts were injected (a) immediately after preforming, (b) after aging 1 day at 25°C., (c) after aging 2 days at 25°C., and (d) after aging 7 days at 25°C. The polymerizations were carried out at 50°C. for 30 minutes and the pertinent data are summarized in Table III below.

TABLE III

			Catalyst Aging Time — Days			
			0	1	2	7
Catalyst	Preforming Monomer	Polymer Yields, Weight %				
5	Control ^(a)	None	21	23	22	25
	A ^(b)	Isoprene	53	65	69	79
	B ^(b)	Butadiene	60	81	87	94

^(a) — "in situ" catalyst addition

^(b) — Mole Ratio, Diolefin:Ce=30:1.

- 10 The catalysts employed immediately after preforming and without aging are not intended as examples of the invention but are included for the purposes of comparison only.

15 While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the claims appendant hereto.

WHAT WE CLAIM IS:—

1. In the process which comprises the polymerization of at least one conjugated diolefin by contacting said conjugated diolefin, under solution polymerization conditions, with a catalyst system comprising (A) a compound selected from organoaluminum compounds containing at least one carbon to aluminum bond, (B) a metallic coordination compound, the metal of which is selected from metals of Group III-B of the Periodic Table referred to herein, and having atomic numbers of 21, 39 and 57 to 71 inclusive and (C) at least one compound containing one or more halide ions, the improvement which comprises preforming and aging the catalyst system with at least one conjugated diolefin in an amount which gives a mole ratio of diolefin to Group III-B metal compound ranging from 0.2/1 to 3000/1.
2. The process according to claim 1 in which the preferred mole ratio of conjugated diolefin to Group III-B metal ranges from 5/1 to 500/1.
3. The process according to claim 1 in which the diolefin polymerized is butadiene 1,3.
4. The process according to claim 1 in which the diolefin polymerized is isoprene.
5. The process according to claim 1 in which the diolefin polymerized is a mixture of butadiene and isoprene.
6. The process according to claim 1

wherein the organoaluminum compound is diisobutylaluminum hydride.

7. The process according to claim 1 wherein the organoaluminum compound is triisobutylaluminum.

8. The process according to claim 1 wherein the Group III-B metal is cerium.

9. The process according to claim 1 wherein the halide ion in the (C) catalyst component is chloride ion.

10. The process according to claim 1 wherein the halide ion in the (C) catalyst component is bromide ion.

11. The process according to claim 1 wherein the atomic ratio of the halide ion to the Group III-B metal ranges from 0.5/1 to 3.5/1.

12. The process according to claim 1 wherein the atomic ratio of the halide ion to the Group III-B metal is substantially 2/1.

13. The process according to claim 1 wherein the polymerization catalyst is preformed in the presence of a conjugated diolefin and is then aged at 0°C. to 100°C. for a period of time ranging from one minute to 30 days.

14. A catalyst composition comprising (A) a compound selected from organoaluminum compounds containing at least one carbon to aluminum bond, (B) a metallic coordination compound, the metal of which is selected from metals of Group III-B of the Periodic Table referred to herein, (C) at least one compound containing one or more halide ions and (D) at least one conjugated diolefin.

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